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**THE TEMPERATURE VARIATION OF HYDROGEN
DIFFUSION COEFFICIENTS IN METAL ALLOYS**

By M.D. Danford

Materials and Processes Laboratory
Science and Engineering Directorate

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16. Abstract <p>Hydrogen diffusion coefficients have been measured as a function of temperature for a few metal alloys using an electrochemical evolution technique. Results from these measurements are compared to those obtained by the time-lag method. In all cases, diffusion coefficients obtained by the electrochemical method are larger than those by the time-lag method by an order of magnitude or more. These differences are attributed mainly to hydrogen trapping.</p>					
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TECHNICAL MEMORANDUM

THE TEMPERATURE VARIATION OF HYDROGEN DIFFUSION COEFFICIENTS IN METAL ALLOYS

INTRODUCTION

The determination of hydrogen diffusion coefficients in metals by the time-lag technique is a permeation method which has often yielded diffusion coefficients too small by some orders of magnitude compared with more recent data obtained by other techniques, such as the evolution method. These differences have been attributed to the effects of surface layers, such as oxide films, which coat the metal surface [1]. In the time-lag technique, an evacuated system is filled with hydrogen gas on one side of a metal membrane, and the build-up of pressure on the other side as the hydrogen diffuses through the membrane is measured as a function of time. From these data, the delay in pressure response due to diffusing hydrogen is obtained and the resulting hydrogen diffusion coefficient is calculated.

In an attempt to understand differences in results for hydrogen diffusion coefficients obtained with the time-lag method and electrochemically measured results obtained by evolution methods, Inconel 718, Waspaloy, Incoloy 903, and pure nickel, which have also been studied by the time-lag technique [2,3,4], have been studied electrochemically using an evolution technique. The amount of hydrogen diffusing to a metal surface is measured as a function of time, and the hydrogen diffusion coefficient is obtained. To accomplish this, it was necessary to employ an autoclave system to contain liquids under pressure at higher temperatures. Inconel 718, Waspaloy, Incoloy 903, and Pratt & Whitney (P&W) 1480 alloy were studied at 25 °C, 75 °C, and 125 °C, while nickel and MAR-M246(Hf) were studied only at 25 °C and 75 °C. Waspaloy was studied in the temperature range of 200 °C to 560 °C by the time-lag technique [3], Inconel 718 at 150 °C to 500 °C [2], Incoloy 903 at 150 °C to 500 °C [2], and nickel at 25 °C to 500 °C [4]. P&W 1480 and MAR-M246(Hf) have not been studied by the time-lag method. The differences between results from the time-lag method and the electrochemical method are discussed and a possible explanation for these differences presented. Results for P&W 1480 and MAR-M246(Hf), which have not been studied by the time-lag method, are also presented.

EXPERIMENTAL

The autoclave system is shown in figure 1 with the silver/silver chloride high temperature reference electrode in the foreground and the platinum counter electrode at the left side of the autoclave. The working electrode containing the sample is in the center of the autoclave. The temperature controller is shown at the left of figure 1. Specimens were studied at 25 °C, 75 °C, and 125 °C. In each case, the potential of the silver/silver chloride electrode was adjusted to maintain a potential of +0.25 V (NHE). The sample holder, or working electrode, employed was an adaptation of that shown in figure 2. The glass electrode holder shown in figure 2 was eliminated,

and the sample holder body was made from virgin Teflon, giving better performance at high temperatures. The metal rod supporting the sample holder body was covered with heat-shrink tubing to prevent contact with the electrolyte. The point of contact of the metal rod with the sample holder body was coated with epoxy cement to prevent entry of the electrolyte into the sample holder. The metal support rod was electrically isolated from the body of the autoclave to give reasonably low blank currents from only the sample in contact with the surrounding electrolyte.

The EG&G-PARC model 350A corrosion measurement console was employed for all measurements in this work. The modified sample holder presented a sample area of 1.0 cm² in contact with the electrolyte solution, in this case 0.1N NaOH. The samples consisted of circular metal disks of 1.59-cm diameter and 0.16-cm thickness. The samples were prepared by wet sanding and degreasing with trichloroethylene. Sample blanks were run at a constant potential of 0.25 V (NHE) for 11,500 seconds for each sample at each temperature with the value of the current being recorded at 500-second intervals.

After blank determinations, samples were electrolytically charged with hydrogen at 150 °C in a salt bath consisting of a molten eutectic mixture of sodium bisulfate and potassium bisulfate. This charging temperature insured an essentially uniform initial hydrogen distribution in the sample after charging. Each sample was charged for 1 hour at a current density of 95 mA/cm². Data for the hydrogen-containing samples were collected in the same manner as those for the blanks, with the currents due only to hydrogen being obtained by subtraction of blank values. After each run, the current versus time data were read to an IBM PC/AT computer for analysis.

CALCULATIONS

For a uniform initial hydrogen distribution in a flat sample where the sample contains a uniform concentration of hydrogen, C_0 , throughout, $C(X,t)$, where X is a particular sample depth and t is a particular time, is given by:

$$C(X,t) = \frac{4C_0}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \sin \frac{(2m+1)\pi X}{L} \exp\left[\frac{-D(2m+1)^2\pi^2 t}{L^2}\right]. \quad (1)$$

Here, L is the sample thickness and D is the diffusion coefficient. The amount of hydrogen desorbed after a time t is given by:

$$Q(t) = Q_{HM}^{\infty} - 0.0957341d \int_0^L C(X,t) dX \quad (2)$$

Here, d is the metal density, and the conversion factor is that necessary to convert from ppm-cm to coulombs/cm². Q_{HM}^{∞} is the total amount of hydrogen initially contained in the sample, and its value is obtained experimentally, as has been previously discussed [5]. In practice, it has been customary to use only the data obtained after a long time (25 to 42 hours) to obtain values of the hydrogen

diffusion coefficients since only the first term of the series in equation (1) is then significant, greatly facilitating the calculations. However, limitations of the plastic sample holders and the high temperature reference electrode precluded containment of the samples for such periods at high temperature. It was necessary to reduce the experiment time to 11,500 seconds and to use the entire series in equation (1) in order to use data at small time.

To obtain the value of the current at a given time, it is necessary to differentiate equation (2) with respect to time, giving:

$$I(t) = 95,734.1d \int_0^L \frac{d}{dt} C(X,t)dX \quad (3)$$

$I(t)$ is thus given in microamps/cm² and the other symbols have the same significance as before. The derivative of $C(X,t)$ with respect to time is given by:

$$\frac{d}{dt} C(X,t) = -\frac{4C_0D\pi}{L^2} \sum_{m=0}^{\infty} (2m+1) \sin \frac{(2m+1)\pi X}{L} \exp \left[\frac{-D(2m+1)\pi^2 t}{L^2} \right] \quad (4)$$

Equations (3) and (4) were incorporated into the general nonlinear least squares program ORGLS [6], the parameters being C_0 and D . For given values of X and t in equation (4), it has been determined that 25 terms of the series are sufficient to give a satisfactory solution to the equation. Values of $C(X,t)$ for a given time were calculated for ten values of X across the sample thickness, ranging from $X=0$ to $X=L$. The integration in equation (4) was performed numerically, using interpolation to make a finer grid and increase accuracy. Fits of the theoretical currents to the observed currents were always very good, but the calculation was slow due to its complexity. However, parameter errors were always small. A comparison of diffusion coefficients obtained by this method at 25 °C with those obtained by measurements after a long time is made in table 1 for some of the metal alloys studied.

RESULTS AND DISCUSSION

In cases where hydrogen diffusion coefficients were obtained at 25 °C, 75 °C, and 125 °C, the three points were fitted by least squares to the Arrhenius equation:

$$\log D = -E/2.303RT + \log D_0 \quad (5)$$

From this procedure, values of the slope, $-E/2.303R$, and intercept, $\log D_0$, were obtained. In the case of nickel 270 and MAR-M246(Hf), where diffusion coefficients were measured at 25 °C and 75 °C, values of the parameters were determined through solution of the simultaneous equations. Values of the parameters obtained are listed in table 2, and compared to those obtained by the time-lag technique for Waspaloy, Incoloy 903, Inconel 718, and nickel 270. Graphs of the electrochemical results, together with those obtained through extrapolation of time-lag results, are shown

in figures 3 to 6. As the figures show, diffusion coefficients for the time-lag technique are always smaller than those for the electrochemical evolution technique. The slopes of the lines obtained by the electrochemical method are about the same as those for the time-lag method, within the experimental error, except for that of Incoloy 903. A comparison of diffusion coefficients at 25 °C by the electrochemical method with those from the time-lag method is made in table 3, and the ratios between results for the two methods are listed. As table 3 shows, the results differ by about three orders of magnitude for Waspaloy and Incoloy 903, two for Inconel 718, and only one for nickel 270, the ratio being only 27. Waspaloy, Incoloy 903, and Inconel 718 trap hydrogen strongly, and contain either niobium or titanium or both, which form very stable hydrides [7]. The order of affinity for hydrogen has been determined to be Ta>Ti>Nb>Hf>V>Cr>Mo, Co, Ni [7]. The values of the ratios strongly suggest that hydrogen trapping plays an important role in the difference between time-lag and electrochemical results. Nickel, which has the smallest ratio, also displays the smallest trapping percentage. In addition, as the order of hydrogen affinities shows, nickel is one of the elements with the smallest hydrogen affinity. Also, the hydrides of nickel are unstable, and are readily decomposed [8].

Values of diffusion coefficients calculated at 537 °C using the Arrhenius relation are listed in table 4. Diffusion coefficients for Inconel 718, Incoloy 903, and P&W 1480 are the smallest at this temperature. Inconel 718 contains about 6 percent of niobium plus titanium, elements which form very stable hydrides. Incoloy 903 contains 1.2 percent Nb, 1.2 percent Ta, and 1.4 percent Ti, all highly stable hydride formers. Further, it is liberally interspersed with carbides of Ti and Ti plus Nb, which have been determined to be high energy hydrogen traps [9]. P&W 1480 contains 12 percent Ta, which has the highest hydrogen affinity of all elements investigated. The stability of these hydrides at higher temperatures is postulated to be primarily responsible for the smaller hydrogen diffusion coefficients at 537 °C.

Typical variation of C_0 , the initial mobile hydrogen concentration in the metal, with temperature is illustrated in table 5 for Waspaloy. As table 5 shows, the value of C_0 increases as the temperature is increased. That is, the amount of mobile hydrogen increases with increasing temperature. This is an expected result, since hydride stability decreases with increasing temperature, and the amount of mobile hydrogen available is therefore greater.

CONCLUSIONS

Hydrogen diffusion coefficients, as measured by an electrochemical evaluation method, are larger by two or three orders of magnitude than those obtained by the time-lag method. Although the formation of oxide films may play a minor role in these differences, it is postulated that the major differences are attributable to hydrogen trapping. Hydrogen trapping has also been set forth as being responsible for similar differences between time-lag results and results obtained with break-through methods [10]. Nickel 270, which displays the lowest ratio of any of the alloys investigated, also has the smallest trapping percentage, and forms unstable hydrides. Smaller hydrogen diffusion coefficients, calculated at 537 °C, are obtained for Inconel 718, Incoloy 903, and P&W 1480, all of which contain elements with high hydrogen affinity.

The amount of mobile hydrogen in metals charged under the same conditions increases with increasing temperature, attributed to the fact that metal hydrides become less stable at higher temperatures. Thus, more hydrogen is available for diffusion.

REFERENCES

1. Ziichner, H.: JIMIS-2, Hydrogen in Metals, p. 101.
2. Robertson, W.M.: Met. Trans., Vol. 8A, November 1977, p. 1709.
3. Perng, T.P., Johnson, M.J., and Alstetter, C.J.: Met. Trans., Vol. 19A, May 1988, p. 1187.
4. Robertson, W.M.: 2. Metallkde, Vol. 64, 1973, p. 436.
5. Zakroczymski, T.: Corrosion, Vol. 38, 1982, p. 218.
6. Busing, W.R., and Levy, H.A.: A General Fortran Least Squares Program, ORNL-TM-271, July 1962.
7. Danford, M.D.: NASA Technical Paper 2882, Januaury 1989.
8. Wollan, E.O., Cable, J.W., and Koehler, W.C.: J. Phys. Chem. Solids, Vol. 12, 1959, p. 206.
9. Pressouyre, G.M., and Bernstein, I.M.: Met. Trans., Vol. 9A, 1978, pp. 1571–1579.
10. Stevens, M.F., and Bernstein, I.M.: Met. Trans., Vol. 20A, May 1989, p. 909.

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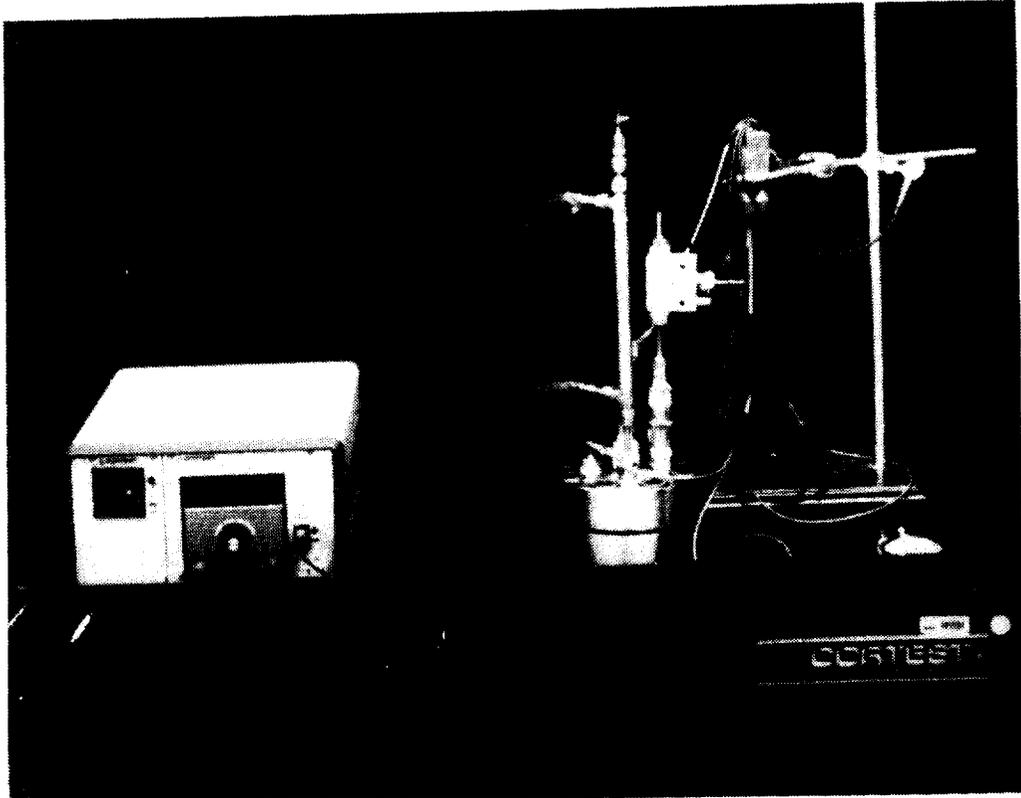


Figure 1. The autoclave system.

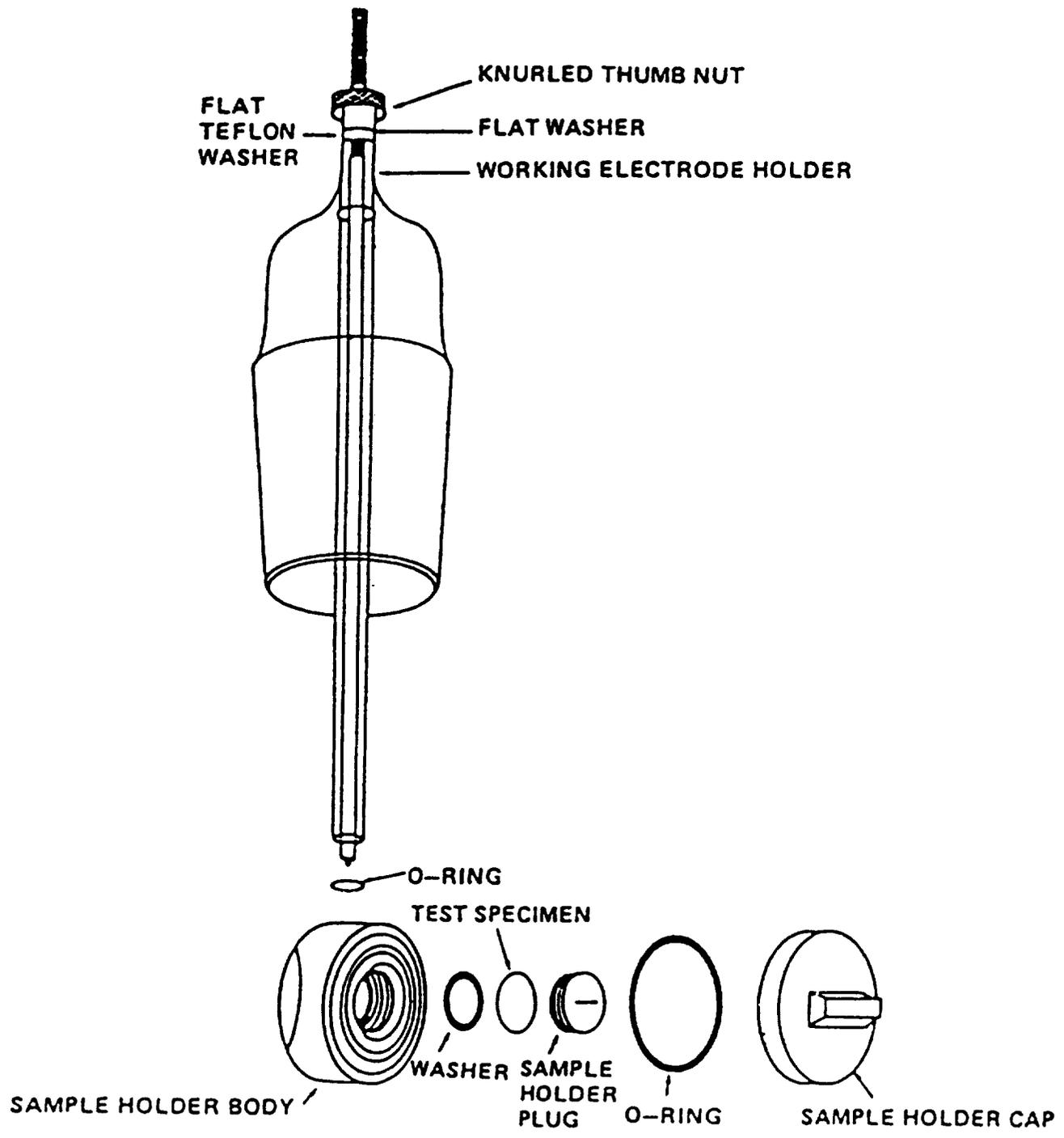


Figure 2. Exploded view of the sample holder.

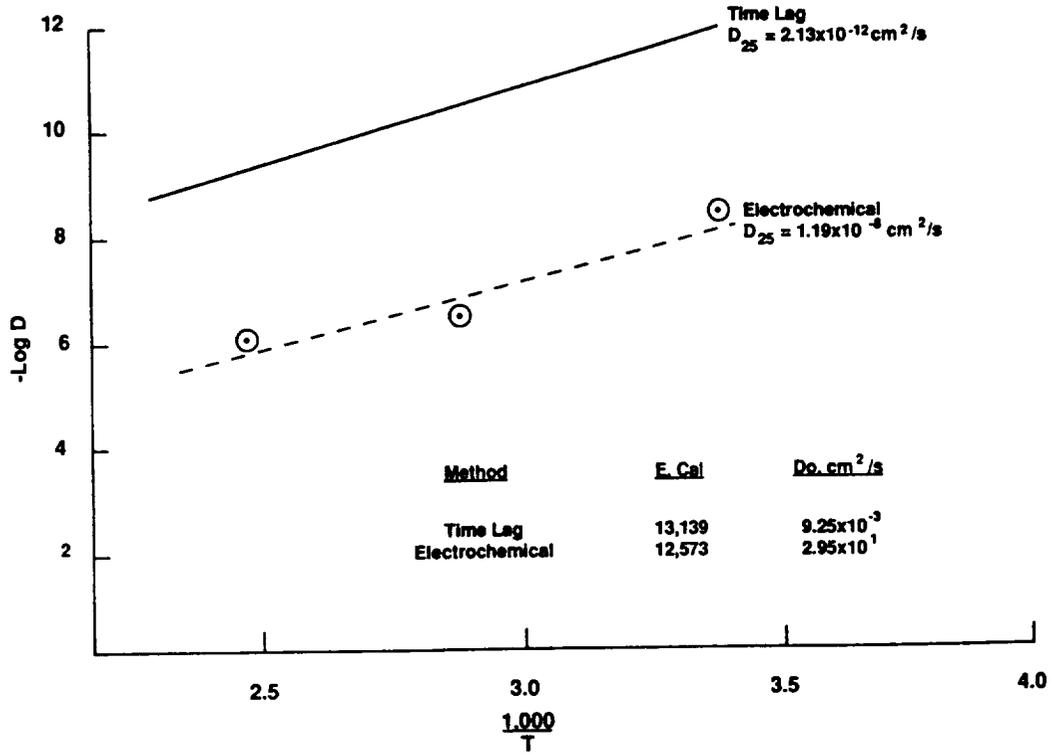


Figure 3. Electrochemical and time-lag curves for Waspaloy.

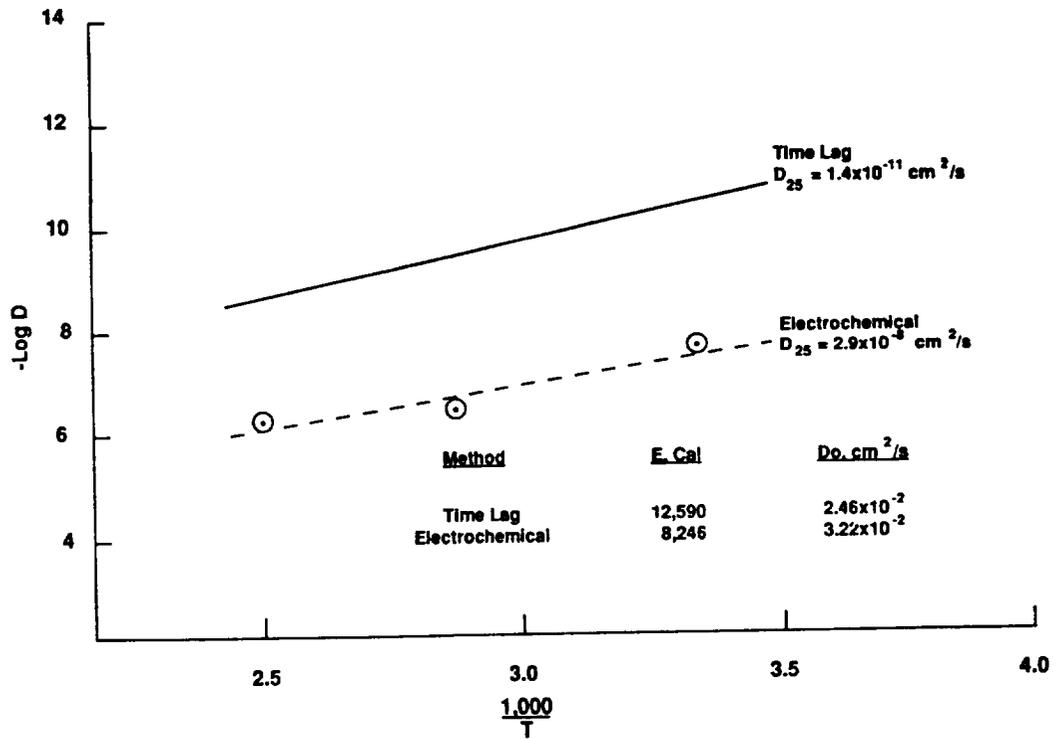


Figure 4. Electrochemical and time-lag curves for Incoloy 903.

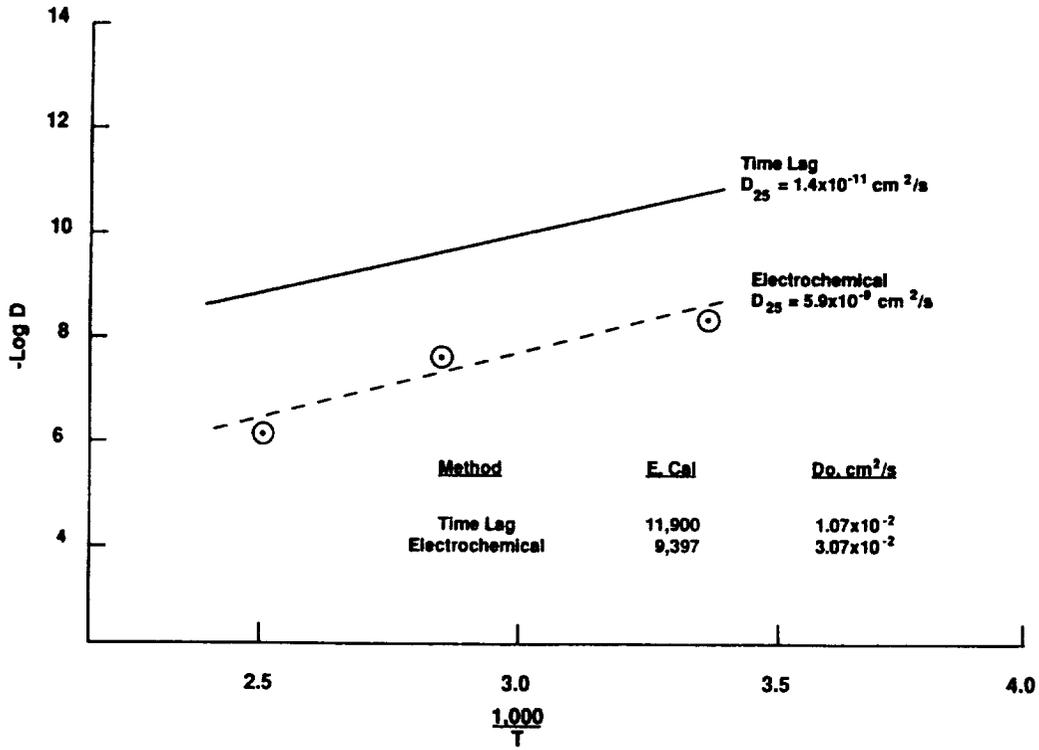


Figure 5. Electrochemical and time-lag curves for Inconel 718.

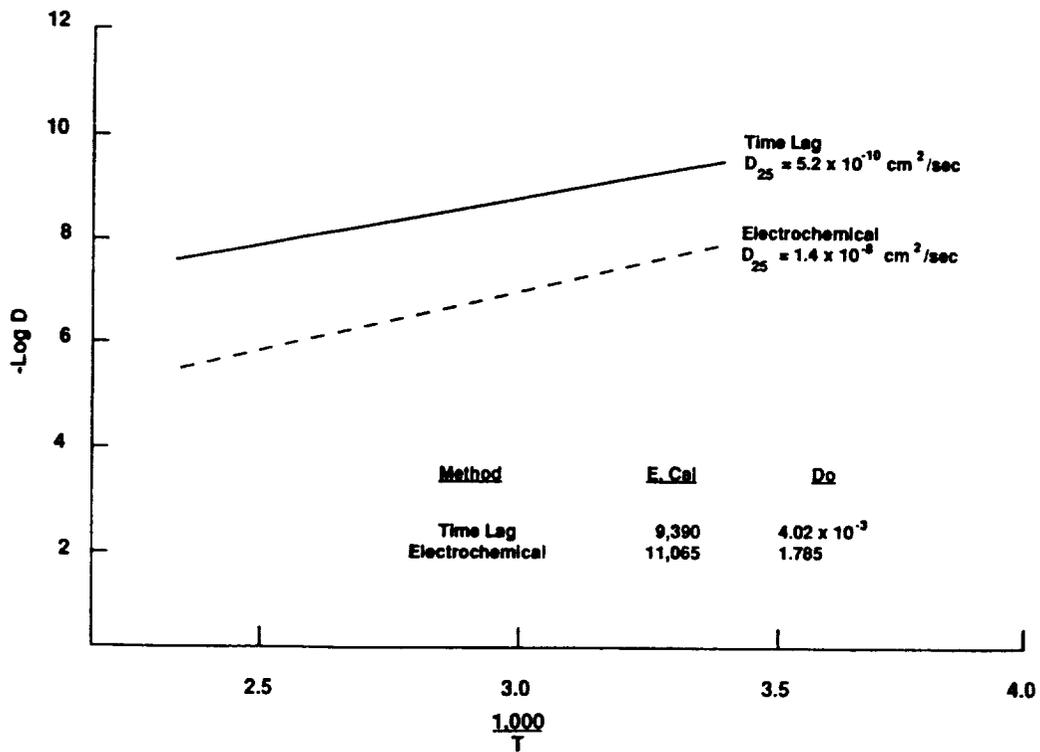


Figure 6. Electrochemical and time-lag curves for nickel 270.

Table 1. Comparison of diffusion coefficients at 25 °C for old and new methods.

<u>Material</u>	<u>New Method</u> DX10 ⁸ , cm ² /s	<u>Old Method</u> DX10 ⁸ , cm ² /s
Incoloy 903	2.94	1.28
Waspaloy	1.19	2.15
Nickel 270	1.37	0.78
P&W 1480	4.07	2.94
MAR-M246 (Hf)	1.36	2.26

Table 2. Comparison of Arrhenius parameters* for electrochemical evolution and time-lag methods.

<u>Material</u>	<u>Electrochemical</u>		<u>Time-lag</u>	
	<u>E</u> cal/K/mole	<u>Do</u> cm ² /s	<u>E</u> cal/K/mole	<u>Do</u> cm ² /s
Waspaloy	12,573	2.95x10 ¹	13,139	9.25x10 ⁻³
Incoloy 903	8,246	3.22x10 ⁻²	12,590	2.46x10 ⁻²
Inconel 718	9,397	3.07x10 ⁻²	11,900	1.07x10 ⁻²
Nickel 270	11,065	1.785	9,390	4.02x10 ⁻³
P&W 1480	7,113	9.36x10 ³	--	--
MAR-M246 (HF)	15,757	4.88x10 ³	--	--

* $D = D_0 \exp(-E/RT)$

Table 3. Comparison of diffusion coefficients at 25 °C for time-lag and electrochemical methods.

<u>Material</u>	<u>Electrochemical</u> cm ² /s	<u>Time-lag</u> cm ² /s	<u>Ratio</u>	<u>%H²Trapping</u> 150 °C
Waspaloy	1.2x10 ⁻⁸	2.13x10 ⁻¹²	5.59x10 ³	56.4
Incoloy 903	2.9x10 ⁻⁸	1.4x10 ⁻¹¹	2.07x10 ³	57.3
Inconel 718	5.9x10 ⁻⁹	1.4x10 ⁻¹¹	4.21x10 ²	81.5
Nickel 270	1.4x10 ⁻⁸	5.2x10 ⁻¹⁰	2.69x10 ¹	29.9

Table 4. Values of diffusion coefficients at 537 °C as obtained from electrochemical method by extrapolation.

<u>Material</u>	<u>D, 537 °C</u> cm ² (sec)
Waspaloy	1.2x10 ⁻²
Incoloy 903	1.9x10 ⁻⁴
Inconel 718	9.0x10 ⁻⁵
Nickel 270	1.9x10 ⁻³
P&W 1480	1.1x10 ⁻⁴
MAR-M246 (Hf)	1.9x10 ⁻³

Table 5. Variation of Co with temperature for Waspaloy. *

<u>Temperature, °C</u>	<u>Co, ppm</u>
25	1.30
75	3.52
125	5.65

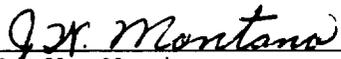
* All samples charged at 150 °C at a current density of 95 mA/cm².

APPROVAL

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By M.D. Danford

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



J. W. Montano
Chief
Corrosion Research Branch



Paul M. Munafa
Chief
Metallic Materials Division



Paul H. Schuerer
Director
Materials & Processes Laboratory

